

Incorporation of triethoxysilyl functionalized Coumarin 4 in sol-gel hosts

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ABSTRACT

A silylated Coumarin 4 (derCoup) laser dye has been incorporated over a large range of concentrations in sol-gel silica composites. Optically transparent films of derCoup and Coumarin 4 (Coup) doped silica were obtained; and their absorption and fluorescence spectra and fluorescence efficiency were measured. Dye extraction was investigated as a function of sol-gel processing conditions. Dye extraction results indicated that prehydrolysis of the derCoup and full hydrolysis of TMOS resulted in films from which the dye could not be extracted, suggesting that all the dye is bonded within the sol-gel matrix. The silylated dye films showed higher fluorescence efficiency at all concentrations with respect to the normal dye film.

1. INTRODUCTION

The past decade has seen great interest in producing a solid-state organic gain medium. Since dye/solvent lasers require pumping systems, and have limited lifetimes due to photo-decomposition and chemical instability, solid state organic media appear attractive for tunable solid state lasers, especially in the visible.

Laser dye molecules have been doped into both polymers and inorganic glasses. Polymer hosts suffer significant photodegradation due to free radical formation of the dye molecules¹. Inorganic hosts appear more attractive because they have high laser damage thresholds. Because of the limited temperature stability of organic lasing dyes, using a low temperature sol-gel process is attractive for incorporating organic molecules within an inorganic host. Numerous lasing dyes, such as rhodamines²⁻⁷ and coumarins⁸⁻¹², have been incorporated within sol-gel hosts of silica, alumina, and organically modified silica (Polycerams). Caging lasing dyes within a sol-gel host has shown improved (but still inadequate) photostability and has permitted high dye concentrations without undesirable

dye aggregation². Dye/host interactions could provide for greater tuning of the fluorescence, improved photostability, reduced photodegradation, and even improved quantum efficiency of the fluorescence.

A number of silylated dyes, such as silylated Disperse Red 1^{13, 14}, silylated para-nitroaniline^{15, 16}, and silylated dinitroaniline (TDP)¹⁷⁻¹⁹, have been incorporated in sol-gel matrices for nonlinear optic applications. Silylated dyes have been used to bond the dye chemically within the matrix.

The use of silylated active molecules seems attractive for laser dye/sol-gel nanocomposites. Increase in the effective molecular rigidity and possible reduction in aggregation could provide for improved quantum yield by limiting nonradiative transitions. Also, it is hypothesized that improved photostability may be achieved due to further reduction of both vibrational and rotational modes of energy dissipation and greater dye isolation. Isolation of the dye molecules limits the interaction between the molecules reducing intersystem crossing to the triplet states and hence reducing decomposition.

The present study has investigated the effects of bonding a fluorescent dye within a sol-gel matrix. A Coumarin 4 (Coum) laser dye was chosen because it has an -OH group which was readily functionalizable to form a silylated dye. Unfunctionalized Coum has been successfully incorporated in sol-gel matrices and its fluorescent properties have been well characterized^{8, 9, 20-22}. In this paper, the absorption and fluorescent properties of Coumarin 4 and a functionalized Coumarin 4 (derCoum) in solvent and sol-gel films are reported. Also, the chemical stability of functionalized and unfunctionalized dye/silica nanocomposites are reported.

2. EXPERIMENTAL

2.1. Preparation of derCoum

7-hydroxy-4-methylcoumarin (Coumarin 4) (Aldrich Chemical Company) was recrystallized and reacted with 3-isocyanatopropyltriethoxysilane (Huls) to obtain O-4-methylcoumarinyl-N-[3-(triethoxysilyl)-propyl]carbamate (derCoum)²³ as shown in Fig. 1. The reaction was carried out in tetrahydrofuran (THF) with a tin catalyst and was monitored by FTIR (Perkin-Elmer 1725x). During the formation of the derCoum, the isocyanate peak (2290 cm^{-1}) disappeared and the urethane peak (1765 cm^{-1}) increased. DSC (Perkin-Elmer DSC-7) also confirmed formation of derCoum by indicating a large change in the melting point, 192 C for Coum and 95 C for derCoum.

2.2. Preparation of sol-gel/dye nanocomposites

DerCoum and Coum were doped at various concentrations in sol-gel derived silica to form thin films. Typically, tetramethoxysilane (TMOS) and H₂O (acidified to 0.15 M HCl) were mixed in a glass vial at a TMOS:H₂O molar ratio of 1:4. Initially, the H₂O was insoluble within the TMOS, but rapid hydrolysis produced a miscible solution within a few minutes. Separately, the dye was dissolved in MeOH. DerCoum was more soluble than Coum in the

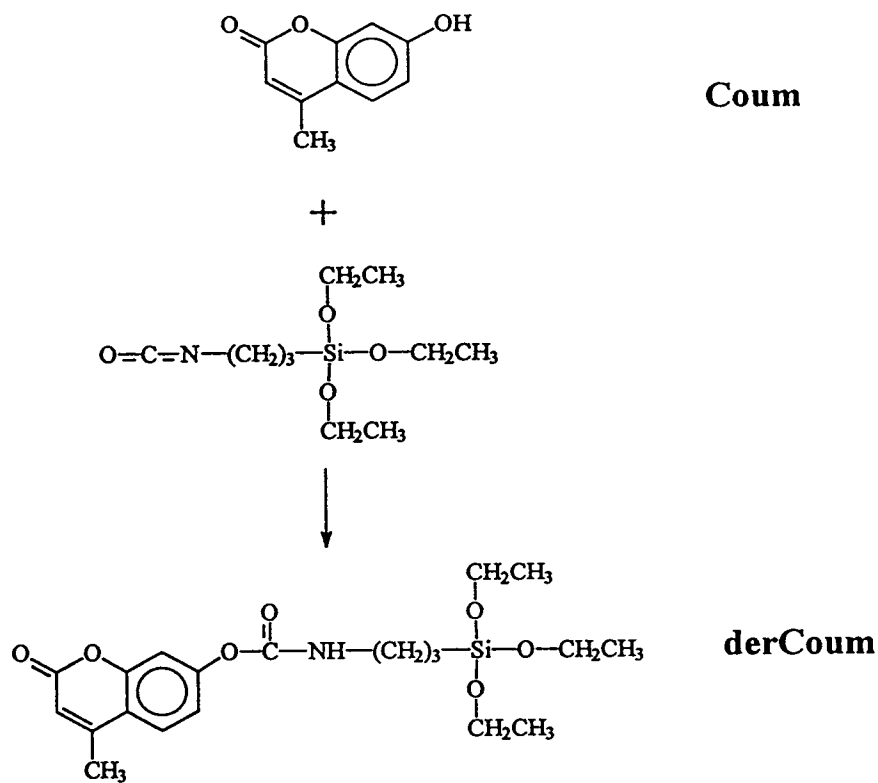


Fig. 1: Synthetic route for derCoul.

solvent. Additional H_2O was added with derCoul solutions at a derCoul: H_2O molar ratio of 1:3. The two solutions were mixed, resulting in a solution with a desired TMOS:dye molar ratio. The solids:solvent ratio of the final solution was maintained at a 1:2 weight ratio for all solutions. The pH of the solutions ranged from 1.8-2.2 depending on the dye concentration. After aging for 24 hrs, the solutions were passed through $0.8\ \mu\text{m}$ filters and spin coated on pre-cleaned microscope slides (Gold Seal) at 2000 rpm for 20 sec. The films were dried at $125\ \text{C}$ for 48 hrs in vacuum. All films were about $0.5\ \mu\text{m}$ as measured with a Dektak II profilometer. All derCoul doped films were transparent, whereas at high concentrations, Coum-doped films appeared slightly cloudy due to crystallization of the Coum dye.

Table 1 indicates the samples made for this study. Note that the derCoul:silica molar ratio was measured taking into account the SiO_2 which results from the silylated dye. Therefore, a 1.0 M composition is a 100% derCoul film. The dye concentration represents the moles of dye per liter of solvent in the sol-gel solution. The dye densities ($\#/\text{cm}^3$) were calculated assuming a skeletal density of $2.05\ \text{gm}/\text{cm}^3$.

Table 1: Laser dye/sol-gel samples investigated.

derCoulm :SiO ₂	Coulm :SiO ₂	Dye Concentration (moles/L)	Dye Density (cm ⁻³)
10 ⁻⁵	10 ⁻⁵	2.0*10 ⁻⁵	2.3*10 ¹⁷
10 ⁻⁴	10 ⁻⁴	2.0*10 ⁻⁴	2.3*10 ¹⁸
10 ⁻³	10 ⁻³	2.0*10 ⁻³	2.3*10 ¹⁹
10 ⁻²	10 ⁻²	2.0*10 ⁻²	2.2*10 ²⁰
0.1	0.1	1.8*10 ⁻¹	1.5*10 ²¹

2.3. Optical characterization

Absorption spectra were measured using a Perkin-Elmer Lambda 3B UV/VIS spectrophotometer. A blank microscope slide was used as a reference for the film spectra.

The samples were pumped at normal incidence with a N₂ laser (Photochemical Research Associates LN1000) at 337 nm with a pulse rate of 6 Hz. The fluorescence spectra were measured using the arrangement shown schematically in Fig. 2. A filter was placed in front of the optical multichannel analyzer (OMA) (EG&G) to block off the 337 nm light. The spectrometer of the OMA was calibrated with a mercury light source.

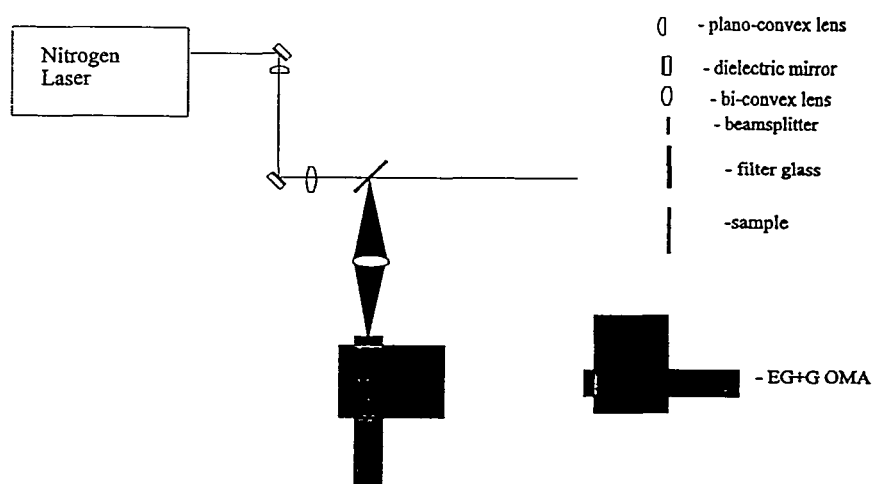


Fig. 2: Schematic of fluorescence measurement apparatus.

2.4. Dye extraction measurements

To characterize the dye incorporation within the sol-gel matrix, dye extraction measurements were performed. The sol-gel films were soaked in THF at 50 C for several days. The THF was kept in an enclosed glass container, and a reflux condenser was used to prevent loss of solvent by evaporation. The samples were periodically removed and the absorbance was measured at the absorption maximum wavelength.

3. RESULTS AND DISCUSSION

3.1. Absorption and fluorescence spectra

Numerous chemical forms of Coum are known depending on its environment (e.g., pH) in solvent and sol-gel hosts^{8, 22, 24}. Three of the ground state forms - neutral, anionic, and cationic - absorb at 320, 365, and 340 nm, respectively, and fluoresce at 400, 455, and 420 nm, respectively. The zwitterionic exciplex form fluoresces at 475 nm. The structure of chemical forms of Coum are illustrated in Fig. 3.

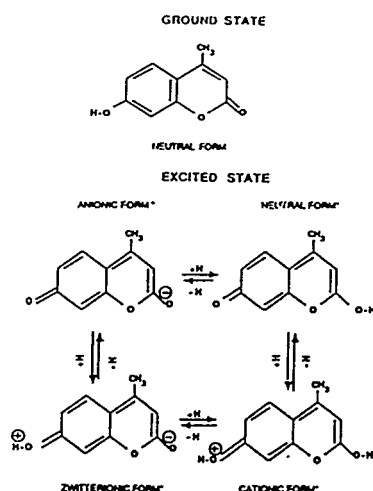


Fig. 3: Structure of different forms of Coum.²²

Fig. 4 shows the absorption and the fluorescence curves for Coum and derCoum dyes at approximately 10^{-5} moles/L in MeOH adjusted to a pH of 2.0 by the addition of HCl. Both of the dyes have very similar absorption spectra with a maximum at 319 nm, indicating the presence of the neutral ground state. The fluorescence of both dyes was also very similar. Multiple fluorescence emission was observed. This is attributed to the presence of the neutral, anionic, and zwitterionic forms in the excited state.

Blue fluorescence was observed in all the dye doped films. The absorption and fluorescence spectra of Coum and derCoum films at 0.01 M appear very similar (Fig. 5). Both absorb near 320 nm and fluoresce in the 430-460 nm range, but the absorption at the tail wavelengths (350-400 nm) of the derCoum films was higher than with Coum films. This

increased absorption is believed responsible for the slight narrowing of the fluorescence bandwidth. Similar results were obtained for the films at other concentrations.

The fluorescence spectra of the solvent samples and the sol-gel films were quite different even though they were measured at similar pH values. This indicates that sol-gel environment greatly affects the fluorescence emission of the dye.

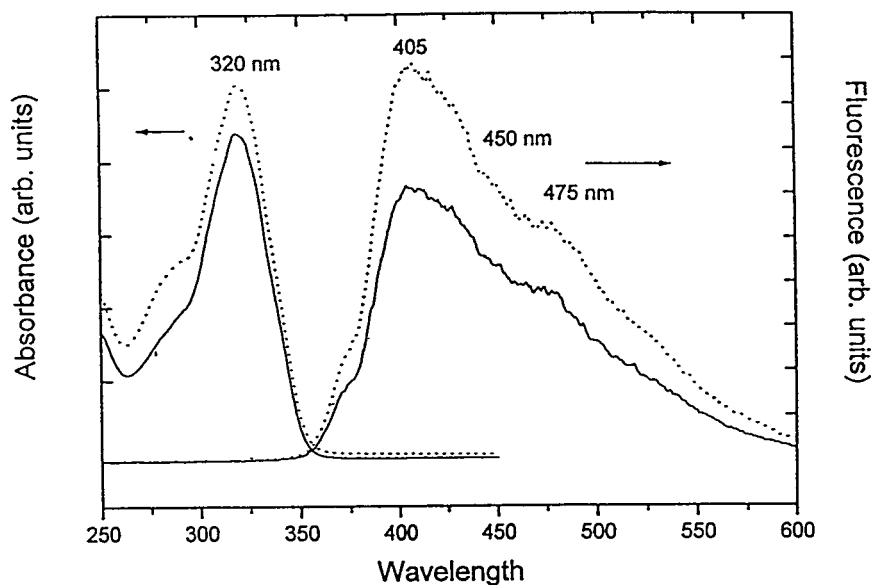


Fig. 4: Absorption and fluorescence curves of Coum (solid) and derCoum (dotted) in MeOH at pH 2.0.

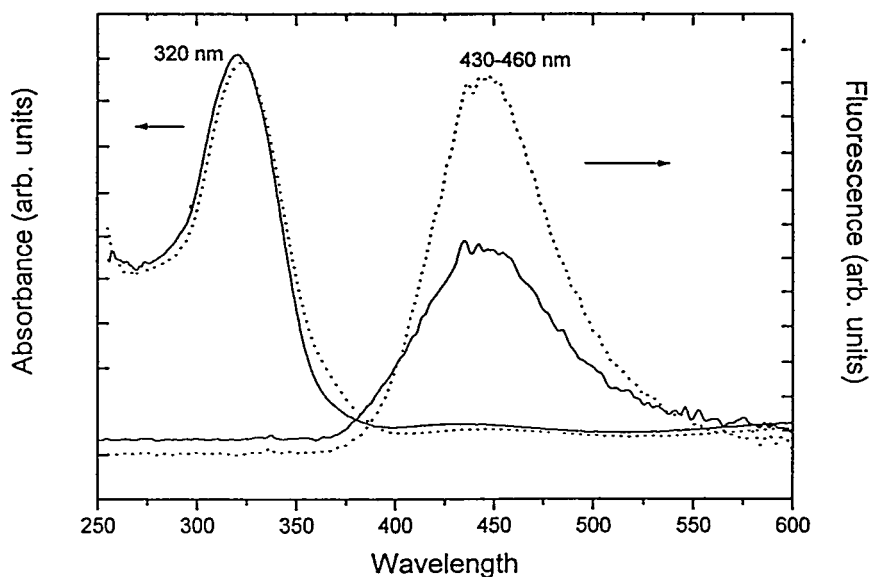


Fig. 5: Absorption and fluorescence curves of Coum (solid) and derCoum (dotted) in dried sol-gel silica films.

3.2. Fluorescence efficiency

The fluorescence quantum yield could not be measured quantitatively with the experimental setup used. The fluorescence efficiency can be described as the ratio of the number of photons emitted to the number of photons absorbed or as:

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc}}$$

where k_f is the fluorescence rate constant, k_{ic} is the internal conversion rate constant, and the k_{isc} is the intersystem crossing rate constant. The relative fluorescence efficiency was determined for the sol-gel films by dividing the area of its fluorescence spectrum by the absorption at the excitation beam wavelength (337nm). Fig. 6 is a plot of this fluorescence efficiency as a function of concentration for the dye/sol-gel films. The fluorescence efficiency was higher for the derCoun films at all concentrations. In contrast, both Coun and derCoun in solvent had essentially the same fluorescence intensity, indicating that both have similar fluorescence efficiencies. The maximum in the fluorescence efficiency was observed at higher concentrations for the derCoun films (0.01 M) than for the Coun films (0.001 M). The silylated dye film showed a 2 fold increase in the fluorescence efficiency at 0.01 M concentration with respect to the normal dye. This improvement is believed to be attributed to the greater rigidity of derCoun [reflecting a reduction of the internal conversion rate constant (k_{ic})], and greater dye isolation [reflecting a reduction of the intersystem crossing rate constant (k_{isc})].

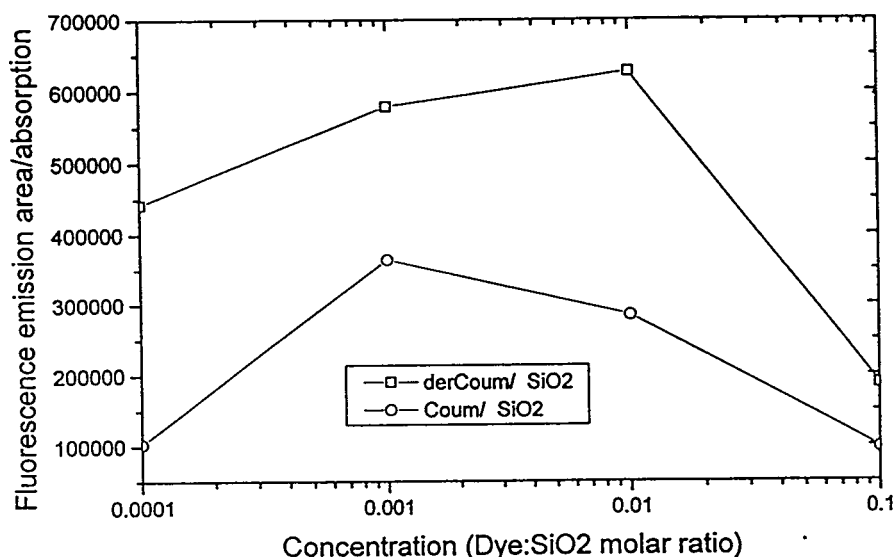


Fig. 6: Fluorescence efficiency as a function of concentration for dye doped films.

3.3. Dye extraction

Dye extraction experiments proved valuable in determining the degree of dye incorporation within the matrix. In Fig. 7, the absorption of the films (normalized to the film absorption before soaking) is plotted as a function of the soak time in THF. The derCoul sample did not show any decline in the absorbance after nearly 4500 min. This indicates that the dye is bonded to the SiO_2 matrix. In contrast, the Coul film showed a decrease in absorption of more than 80% within 1500 min of soaking, indicating substantial dye loss.

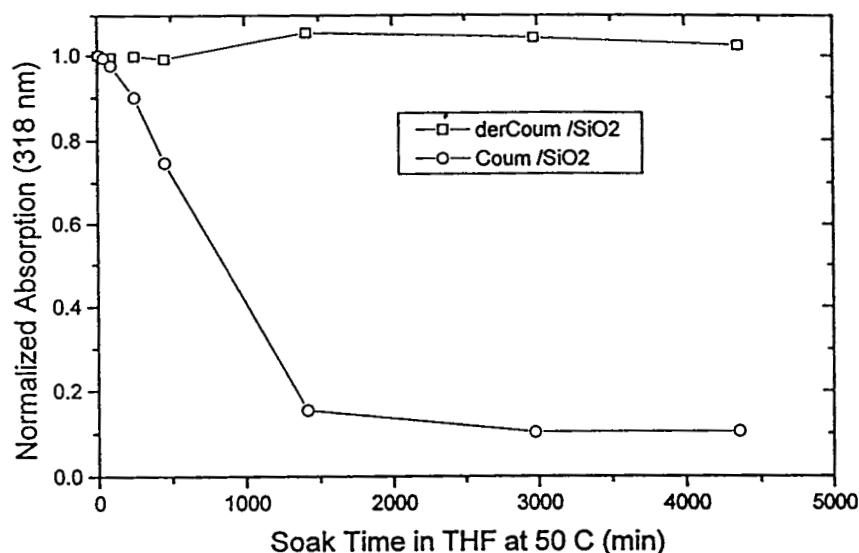


Fig. 7: Dye extraction of derCoul and Coul films.

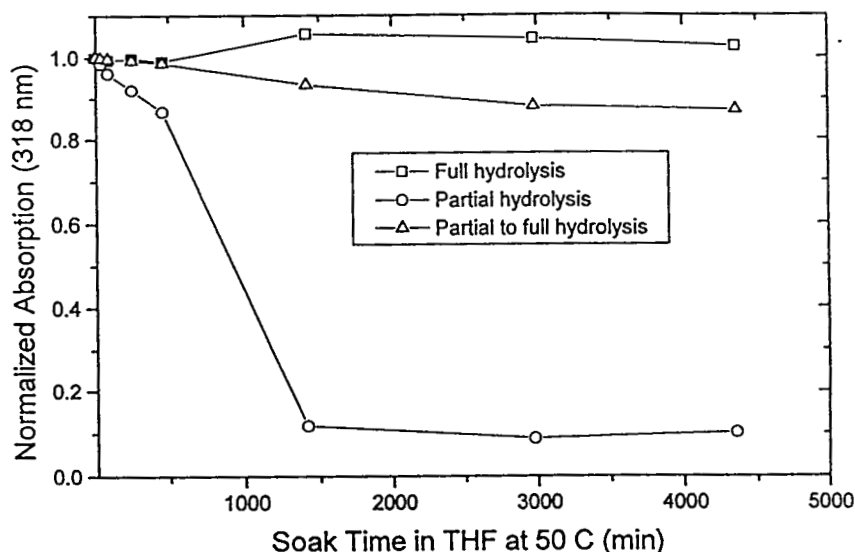


Fig. 8: Dye extraction of derCoul / SiO_2 films at various TMOS: H_2O ratios.

The leachability of the dye from its hosts depend significantly on the processing conditions (e.g., order of precursor mixing, hydrolysis time and water content). Prehydrolysis of the derCoup before mixing with TMOS resulted in films in which the derivatized dye could not be removed (Fig. 7). Complete hydrolysis of derCoup with H₂O took about 45-60 minutes, determined by monitoring the -OH band with FTIR. Such hydrolysis is slow compared with the hydrolysis of TMOS. Prehydrolyzing the slowest hydrolyzing species resulted in greater dye-silica condensation.

The water content also played a large role in the incorporation of derCoup within the sol-gel films (Fig. 8). Large dye loss occurred with a solution processed under partial hydrolysis (TMOS:H₂O=1:2), while no dye loss was observed with full hydrolysis (TMOS:H₂O = 1:4). For other conditions, where the solution was processed under partial hydrolysis and additional water was periodically added to reach stoichiometric water content, slight dye loss was observed. The more permanent dye incorporation at high water content is attributed the greater hydrolysis of the dye and TMOS, resulting in greater condensation of the dye with the silica matrix.

In all variations of processing explored, the Coup dye was always almost completely extracted from the film within 1500 min of soaking. With solutions processed under full hydrolysis conditions, Coup was extracted more slowly than under partial hydrolysis conditions.

These results indicate that under proper processing conditions, the silylated dye can be incorporated within a sol-gel matrix to provide a more chemically stable material than with a normal dye. This allows for the incorporation of large concentrations of organic species while maintaining high chemical and environmental stability.

4. CONCLUSIONS

Coup and silylated Coup laser dyes have been successfully incorporated within sol-gel silica composites over a large range of concentrations. Absorption and fluorescence spectra of the two dyes were very similar, indicating that the functionalization of the dye did not alter its fluorescent properties. Under proper processing conditions, derCoup could not be removed from the film through solvent extraction at elevated temperatures, indicating that the derCoup was completely bonded within the matrix. In contrast, large dye loss was observed in Coumarin 4 films under all processing conditions. The derCoup films show a higher fluorescence efficiency at all concentrations than the Coup films. This is attributed to the greater rigidity and isolation of the silylated dye within its host.

5. ACKNOWLEDGEMENTS

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